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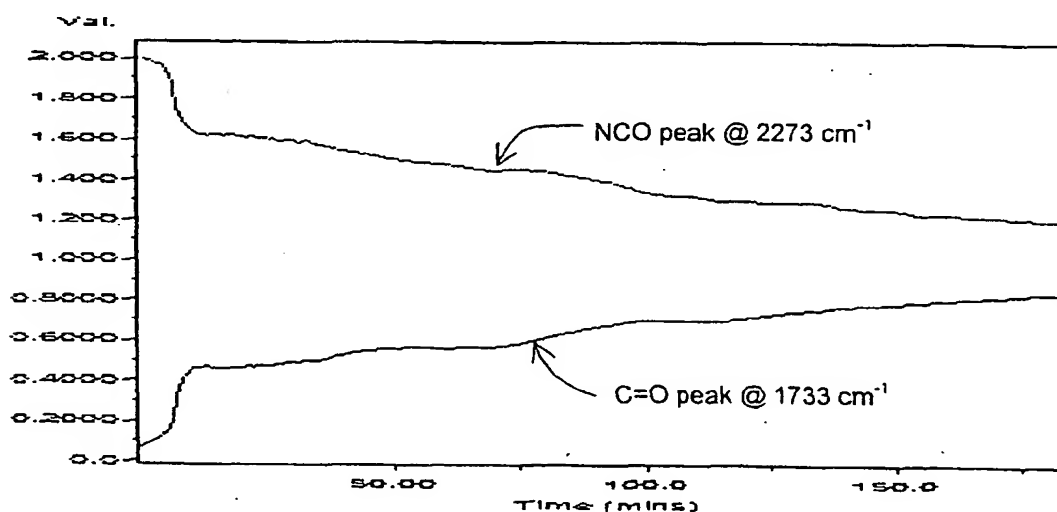
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(54) Title: CATALYSTS AND CURABLE COMPOSITIONS

Catalyst of Example 3



(57) Abstract: The invention provides a compound suitable for use as a catalyst for the formation of urethanes and ureas comprising the reaction product of (i) an alkoxide, condensed alkoxide or halo-alkoxide of titanium zirconium, hafnium or aluminium or a mixture thereof, and (ii) a complexing compound selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols.

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Catalysts and curable compositions

This application concerns catalyst compositions, curable materials containing catalyst compositions and methods for their preparation.

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Catalyst compositions comprising complexes of metals such as titanium are well known for catalysing the formation of polyurethanes, epoxides and polyolefins.

One suitable catalyst composition for catalysing the curing of polyisocyanate materials is disclosed in PCT Application WO 97/17388. This composition comprises a Group IVB metal compound, preferably a titanium chelate, optionally in combination with a compatibilising compound and/or conventional release agents.

US-A-5846897 discloses zirconium compounds with diketones or alkylacetoacetates which catalyse the isocyanate – hydroxy reaction having the chemical structure: Me (X1, X2, X3, X4) wherein Me is zirconium (Zr) or hafnium (Hf) and X1, X2, X3, and X4, are the same or different and selected from the group consisting of a diketone and an alkylacetoacetate having the structures: $R_1COCH_2COR_2$ and $R_1OCOCH_2COR_2$ wherein each of R_1 and R_2 is a branched or linear C1 -C20 hydrocarbon and at least one of X1, X2, X3, and X4 is a diketone with structure (II) wherein the total number of carbons in $R_1 + R_2$ is at least 4.

International Patent Application WO 00/02855 discloses that certain compounds of Group IVB metals can be used to cure isocyanate and polyisocyanate compositions and these compositions are very stable on prolonged storage and economical when used for binding lignocellulosic material. The compounds disclosed are complexes of titanium, zirconium and/or hafnium and an acetoacetate ester in which the molar ratio of Ti or Hf to acetoacetate ester is in the range 1 : 2.5 to 1:10 or the molar ratio of Zr to acetoacetate ester is in the range 1 : 4.5 to 1 : 10 and the acetoacetate ester is an ester of an alcohol containing 1 to 6 carbon atoms.

According to the invention, we provide a compound suitable for use as a catalyst for the formation of urethanes, ureas and epoxy resins comprising the reaction product of (i) an alkoxide, condensed alkoxide or haloalkoxide of titanium zirconium, hafnium or aluminium or a mixture thereof, and (ii) a complexing compound having a hydroxy group which is capable of reacting with the metal compound of (i) and which is selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols.

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The compound is especially useful as a catalyst for the reaction of an isocyanate with an alcohol to form a urethane, especially for polyurethane synthesis or with an amine to form a urea or polyurea compound. The compound is also useful to catalyse the reaction between epoxy groups and hydroxy or amine groups to form epoxy resins.

According to a second aspect of the invention we provide a catalyst composition comprising a compound comprising the reaction product of

- 10 (i) an alkoxide, condensed alkoxide or halo-alkoxide of titanium zirconium, hafnium or aluminium or a mixture thereof, and
- (ii) a complexing compound having a hydroxy group which is capable of reacting with the metal compound of (i) and which is selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives,
- 15 hydrazones and substituted phenols.

According to a further aspect of the invention we provide a curable composition comprising at least one polyisocyanate compound, a compound which is capable of reacting with said polyisocyanate compound to form a polymer and a compound comprising the reaction

- 20 product of
- (i) an alkoxide, condensed alkoxide or haloalkoxide of titanium zirconium, hafnium or aluminium or a mixture thereof, and
- (ii) a complexing compound having a hydroxy group which is capable of reacting with the metal compound of (i) and which is selected from the list comprising oximes, hydroxy-Schiff
- 25 bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols.

The alkoxide of titanium zirconium, hafnium or aluminium has the formula $M(OR)_n$ where M represents the metal, R is an alkyl group, and $n = 3$ or 4 . Each R is preferably the same but may be different from one or each other R. More preferably, R contains 1 to 6 carbon atoms and particularly suitable alkoxides include tetra-methoxytitanium, tetra-ethoxytitanium, tetra-isopropoxytitanium, tetra-n-propoxytitanium, tetrabutoxytitanium, tetra-propoxyzirconium, tetra-butoxyzirconium, tetra-n-propoxyhafnium and tetra-n-butoxyhafnium.

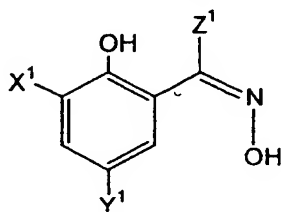
35 Condensed alkoxides of titanium, zirconium or hafnium can be represented by the general formula $RO[M(OR)_2O]_zR$, wherein M and R have the same meaning as discussed above and z is an integer. Generally, these condensed alkoxides consist of a mixture containing compounds of the above formula with z having a range of values. Preferably z has an

average value in the range 2 to 16 and, more preferably, in the range 2 to 8. A condensed alkoxide is usually prepared by the controlled addition of water to an alkoxide, followed by removal of alcohol which is displaced. Suitable condensed alkoxides include the compounds known as polybutyl titanate, polybutyl zirconate and polyisopropyl titanate.

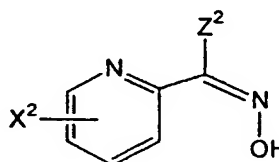
- 5 Mixed halo-alkoxides of titanium, zirconium and hafnium can be represented by the general formula $MX_2OR_{(n-z)}$ wherein X is a halogen atom, preferably Cl, M and R have the same meaning as discussed above, z is an integer and n = 3 or 4.

- The oxime, hydroxy-Schiff base, 8-hydroxyquinoline derivative, 10-hydroxybenzo-[h]-
 10 quinoline derivatives, hydrazone or substituted phenol (hereinafter referred to as the "complexing compound") forms, following deprotonation, an anionic ligand which replaces one or more of the alkoxide groups. These complexing compounds all have the capability of binding to the metal both covalently and also of forming a second covalent or co-ordinating bond to the metal, by means of a second hydroxyl group or an alternative
 15 electron donor, usually in the form of an N atom. Some or none of the original alkoxide groups may remain bonded to the metal following reaction with the complexing compound. Any alkoxide groups remaining on the metal may, optionally, be displaced by reacting the resulting complex with an alcohol, such as phenol for example to form a complex containing an alkoxy group which is different from the alkoxy groups in the metal alkoxide starting
 20 material. These compounds are included as compounds of the invention, even when the final product contains an alkoxy group which would not have formed a titanium alkoxide which could have reacted with the complexing compound to form a compound of the invention.

- 25 Preferred oximes are aryl-substituted (including polycyclic aryl-), aromatic or heterocyclic oximes of Formula 1 or Formula 2,



Formula 1

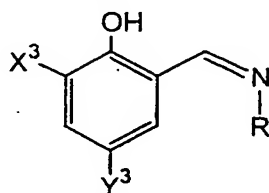


Formula 2

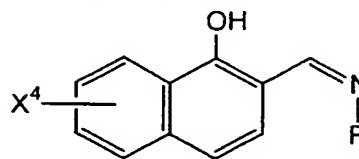
- in which X¹, Y¹ and X², which may be the same or different, are selected from H, alkyl (preferably C₁ – C₆ alkyl, e.g. t-butyl), alkoxy, NO₂, halogen, amino (including alkylamino).
 30 When the oximes are polycyclic aryl-substituted oximes such as naphthalene derivatives for example, Formulas 1 and 2 are amended accordingly.

Z¹ and Z² may be selected from H, or an alkyl aryl or pyridyl group, any of which may be substituted or unsubstituted.

The hydroxy-Schiff bases useful in the invention are of general Formula 3 or 3a:



Formula 3



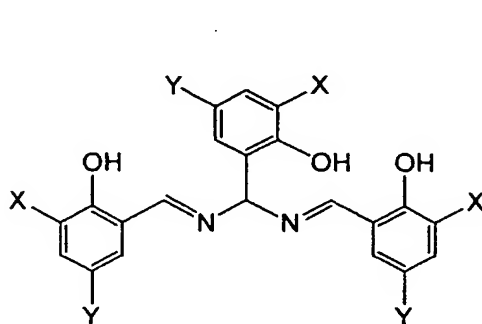
Formula 3a

where each X³ and Y³ may be the same or different, and is selected from H, alkyl

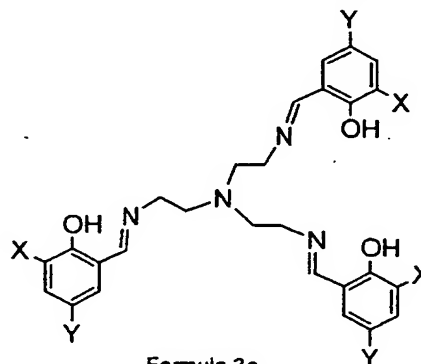
- 5 (preferably C₁ – C₆ alkyl, e.g. t-butyl), alkoxy, NO₂, halogen, amino (including alkylamino) and R is substituted or unsubstituted alkyl (including cycloalkyl), aryl, aryloxy, alkoxy, or a polycyclic group such as quinolyl. When R is substituted alkyl or aryl, the substituents may be selected from alkyl, alkoxy, nitro, halogen or an and there may be one or more than one substituent which may be the same or different from each other. Some useful examples of
- 10 R include isopropyl, adamantyl, ethyl phenyl, phenyl, perfluorophenyl, alkoxyphenyl, bisphenyl, 2,4,6-trimethylphenyl, 2,6 diisopropyl phenyl, 2,4,6-tri-tert-butylphenyl, triphenylmethyl, 2,4,6-triphenylphenyl.

The Schiff bases of the invention include dimeric and trimeric Schiff bases, in which R in

- 15 Formula 3 or 3a comprises a linking group which is linked to a second or third Schiff base moiety which is preferably of the same composition as the other Schiff base moieties in the molecule. The linking group preferably contains between 1 and 6 atoms which are normally selected from C, N and O. The linking group may be substituted or form part of a longer chain or ring structure. Examples of dimeric and trimeric Schiff bases are shown in
- 20 Formula 3b and 3c in which X and Y are selected from the groups listed for X³ and Y³.



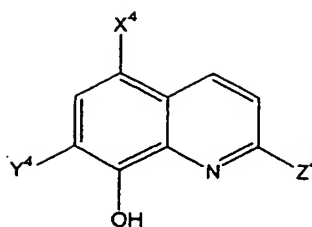
Formula 3b



Formula 3c

The 8-hydroxyquinoline derivatives useful in the invention have the general formula 4:

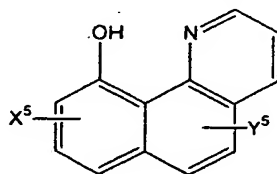
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Formula 4

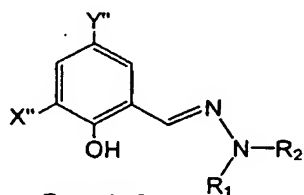
- Where X^4 and Y^4 are, independently H, halogen, NO_2 , alkyl or alkenyl and Z^4 is H or alkyl. Some examples of useful 8-hydroxyquinoline derivatives include 8-hydroxyquinoline, 8-hydroxyquinoline, 5-chloro-8-hydroxyquinoline, 5,7-dichloro-8-hydroxyquinoline, 5-chloro-8-hydroxy-7-iodoquinoline, 8-hydroxy-5-nitroquinoline, 5,7-dibromo-8-hydroxyquinoline, 5,7-dichloro-8-hydroxy-2-methylquinoline, 5,7-dibromo-8-hydroxy-2-methylquinoline, 7-allyl-8-hydroxyquinoline.

- 10 The 10-hydroxybenzo-[h]-quinoline derivatives are of the general formula 5 in which X^5 and Y^5 are, independently H, halogen, NO_2 , alkyl or alkenyl.

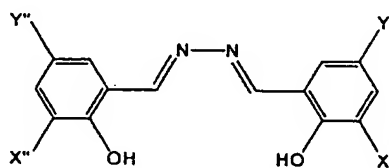


Formula 5

- Suitable hydrazones are aromatic hydrazones, which may be unsubstituted or substituted at either the aromatic ring or the N atom. Therefore these suitable hydrazones have the following general formula 6:



Formula 6



Formula 7

- X'' and Y'' are selected from H, (optionally substituted) alkyl (e.g. $\text{C}_1 - \text{C}_6$ alkyl, such as t-butyl or i-propyl), alkoxy, for example methoxy, aryl, NO_2 , or (optionally substituted) amino. R_1 and R_2 may be H, alkyl or aryl or may be together another hydrazone derivative. In this latter case the molecule is preferably symmetrical so that the two hydrazone derivatives are the same. An example of such a molecule is shown as Formula 7. Polycyclic analogues of these hydrazone derivatives are also included in the suitable hydrazone species for the invention.

Some members of the class of substituted phenols are included hereinbefore either implicitly or explicitly in another class of complexing agents. Other substituted phenols having substituents which include a N, O or S group which can coordinate to a metal atom may also be used as complexing compounds for the invention. Such substituents include

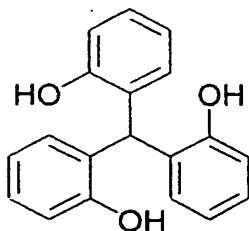
5 hydroxy, hydroxyalkyl, amino, aminoalkyl, oxazole and thiazole- containing groups. The phenol may additionally contain other substituents such as (optionally substituted) alkyl, (e.g. C₁ – C₆ alkyl, such as t-butyl or i-propyl), alkoxy, for example methoxy, aryl or NO₂.

Suitable substituted phenols therefore include but are not limited to 2,4-di^tbutyl-6-amino
 10 phenol, 2,4,6-hydroxymethylphenol, 2-benzoxazol-2-yl-phenol, 2-benzothiazol-2-yl-phenol.

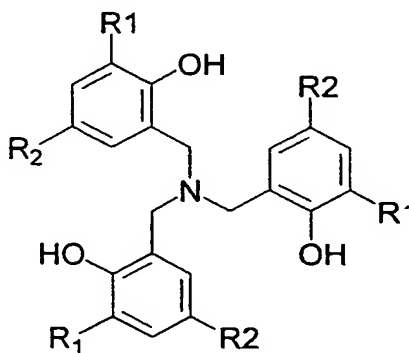
The phenol may be substituted by a phenol derivative. In this case it is preferable that the phenol substituent is of a similar composition to the substituted phenol itself or is joined to the substituted phenol by a symmetrical bridging group, so that the resulting molecule is

15 symmetrical. Examples of such a substituted phenol is 4,4'-methylene-bis(2,6-di^tbutylphenol), 2,2'-methylene bis(6-^tbutyl-4methylphenol), 2,2'-ethylidene bis (4,6-di-*tert*-butyl phenol), and compounds of these bisphenols where the metal M is zirconium or hafnium have not been demonstrated in the prior art. More than one such substituent may be present to provide trisphenol-type compounds such as those illustrated in formulae 8 &

20 9.



Formula 8



Formula 9

R¹ and R² in Formula 9 are each, independently, selected from H, aryl, alkyl, NO₂, amino or a halogen.

25

The compounds of the invention may be made by combining a solution of the complexing compound in an inert atmosphere with the alkoxide, condensed alkoxide or halo-alkoxide of titanium zirconium, hafnium or aluminium, with heating to reflux if necessary. The solid complexes may be purified and isolated by standard synthetic techniques such as

30 crystallisation or precipitation and recrystallised if necessary.

The compounds of the invention may comprise one or more than one metal atom. The complexing compounds, being capable of forming more than one bond with a metal atom, may form bridges between metal atoms to form larger molecules. For example, in a complexing compound containing more than one hydroxy group, each may form a bond to
5 the same or a different metal atom. In this way the architecture of the compound of the invention may be controlled by careful selection of a complexing compound of appropriate functionality.

The catalysts of the invention are useful catalysts for the formation of bonds between an
10 isocyanate group and a group which is reactive with an isocyanate group such as a hydroxy group, especially urethane bonds, most especially as curing agents in polyisocyanate / polyol compositions for polyurethane manufacture. Isocyanate compositions which may be cured using catalysts of this invention may be any organic polyisocyanate compound or mixture of organic polyisocyanate compounds, provided said compounds have at least 2
15 isocyanate groups. Organic polyisocyanates include diisocyanates, particularly aromatic diisocyanates, and isocyanates of higher functionality.

Examples of organic polyisocyanates include aliphatic isocyanates such as hexamethylene diisocyanate; and aromatic isocyanates such as m- and p-phenylene diisocyanate, tolylene-
20 2,4- and tolylene- 2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, chlorophenylene- 2,4-diisocyanate, naphthylene-1,5-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'- diisocyanate-3,3'-dimethyl-diphenyl, 3-methyldiphenylmethane-4,4'-di- isocyanate and diphenyl ether diisocyanate; and cycloaliphatic diisocyanates such as cyclohexane-2,4- and -2,3-diisocyanate, 1-methylcyclohexyl-2,4- and -2,6-diisocyanate and mixtures thereof and
25 bis-(isocyanatocyclohexyl)methane and triisocyanates such as 2,4,6-triisocyanatotoluene and 2,4,4-tri- isocyanatodiphenylether.

Modified polyisocyanates containing isocyanurate, carbodiimide or uretonimine groups may be employed in conjunction with the organometallic complexes of the invention as well.
30 Further blocked polyisocyanates, like the reaction product of a phenol or an oxime and a polyisocyanate, may be used, having a deblocking temperature below the temperature applied when using a polyisocyanate composition.

The organic polyisocyanate may also be an isocyanate-ended prepolymer made by
35 reacting an excess of a diisocyanate or higher functionality polyisocyanate with a polyol.

Water-emulsifiable organic polyisocyanates like those described in GB-A-1444933, in EP-

A-516 361 and in WO93/03082 can also be used.

Mixtures of isocyanates may be used in conjunction with the organometallic composition of the invention, for example a mixture of tolylene diisocyanate isomers such as the
5 commercially available mixtures of 2,4- and 2,6-isomers and also the mixture of di- and higher polyisocyanates. Polyisocyanate mixtures may optionally contain monofunctional isocyanates such as p-ethyl phenylisocyanate.

Such mixtures are well-known in the art and include the crude phosgenation products
10 containing methylene bridged polyphenyl polyisocyanates, including diisocyanate, triisocyanate and higher polyisocyanates together with any phosgenation by-products.

Preferred isocyanates to be used in conjunction with the organometallic complexes of the present invention are those wherein the isocyanate is an aromatic diisocyanate or
15 polyisocyanate of higher functionality such as a pure diphenylmethane diisocyanate or a mixture of methylene bridged polyphenyl polyisocyanates containing diisocyanates, triisocyanates and higher functionality polyisocyanates.

Methylene bridged polyphenyl polyisocyanates are well known in the art. They are
20 prepared by phosgenation of corresponding mixtures of polyamines. For convenience, polymeric mixtures of methylene bridged polyphenyl polyisocyanates containing diisocyanate, triisocyanate and higher functionality polyisocyanates are referred to hereinafter as polymeric MDI. Polyisocyanates suitable for use with the organometallic complexes of the invention include SUPRASEC™ DNR, SUPRASEC™ 2185, RUBINATE™
25 M and RUBINATE™ 1840, all available from Huntsman ICI Polyurethanes..

Preferably the polyisocyanate is liquid at room temperature.

The isocyanate reactive compound is preferably a polyol suitable for forming polyurethanes
30 when reacted with an isocyanate compound in the presence of a catalyst of the invention including those polyols known to the skilled person for the manufacture of polyurethanes and like compounds. These include polymeric polyols such as polyether polyols, polyester polyols, polyolefin polyols, polycarbonate polyols and polymer modified polyols.

35 Useful polymeric polyols are those having at least two isocyanate-reactive groups and include those generally known in the art, such as polyols and polyamines. The polymeric polyol composition preferably comprises about 50 to about 100% and preferably about 75 to about 90% of a polyoxyethylene-terminated polyoxypropylene polyol. This polymeric

polyol should have a nominal hydroxyl functionality of about 2 to 6, preferably 2 to 3 and a total oxyethylene content of about 10 to 21%, preferably about 12 to 20%. Useful polymeric polyols have a hydroxyl equivalent weight of about 700-3000, preferably about 1,500 to 2,500, and more preferably about 1,700 to 2,000. When used, the polyoxyethylene-terminated polyoxypropylated polyol preferably also contains less than about 2% of internal oxyethylene units and should comprise at least 90% by weight of oxypropylene and oxyethylene units.

Polyether polyols which may be used include products obtained by the polymerization of a cyclic oxide, for example ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran in the presence, where necessary, of polyfunctional initiators.

Especially useful polyether polyols include polyoxypropylene diols and triols and poly(oxyethylene-oxypropylene) diols and triols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to di- or trifunctional initiators as fully described in the prior art. Mixtures of the said diols and triols can be particularly useful. Other particularly useful polyether polyols include polytetramethylene glycols obtained by the polymerization of tetrahydrofuran.

Polyester polyols which may be used include hydroxyl-terminated reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, cyclohexane dimethanol, bis(hydroxyethyl)terephthalate, glycerol, trimethylolpropane, pentaerythritol or polyether polyols or mixtures of such polyhydric alcohols and polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride, dimethyl terephthalate or mixtures thereof. Polyesteramides may be obtained by the inclusion of amino alcohols such as ethanolamine in polyesterification mixtures. Polythioether polyols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids.

Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Polyacetal polyols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde or by polymerizing cyclic acetals.

Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane polyols include polydimethylsiloxane diols and triols.

- 5 Other polyols which may be used comprise dispersions or solutions of addition or condensation polymers in polyols of the types described above. Such modified polyols, often referred to as "polymer" polyols have been fully described in the prior art. Polyoxyalkylene polyols containing from 5 to 50% of dispersed polymer are particularly useful. Particle sizes of the dispersed polymer of less than 50 microns are preferred.
- 10 Other useful isocyanate-reactive polymers include polymeric polyamines, especially diamines and triamines, corresponding to the above-described polymeric polyols. Suitable polyamines of polyether polyols are those described, for example, in U.S. Pat. No. 3,654,374 or are obtained by the cyanoethylation of polyols followed by hydrogenation.
- 15 Polyoxypropylene diamines and triamines and mixtures thereof are preferred. Also useful are polymers containing both amino and hydroxyl groups obtained by the partial amination of polyols. Further isocyanate-reactive polymers include imino-functional polymers, such as polymers described in U.S. Pat. No. 4,794,129 together with methods for their preparation and enamine functional polymers which may be prepared either from secondary amine
- 20 terminated resins (i.e. polyethers) by reaction with ketones/aldehydes having one or more alpha hydrogens, or by reacting ketone/aldehyde terminated resins (bearing alpha hydrogens) with secondary amines, providing for removal of the water formed in the reactions.
- 25 A composition containing an organometallic composition of the present invention and a polyisocyanate and compounds reactive therewith may further comprise conventional additives such as diluents, flame retardants, blowing agents, release agents, water, coupling agents, lignocellulosic preserving agents, fungicides, waxes, sizing agents, fillers, colourants, impact modifiers, surfactants, thixotropic agents and other binders like
- 30 formaldehyde condensate adhesive resins and lignin.

- The catalysts of the present invention are useful for the manufacture of polyurethane foams, flexible or rigid articles, coatings, adhesives, elastomers, sealants, thermoplastic polyurethanes, and binders e.g. for oriented strand board manufacture. The catalysts of the
- 35 present invention may also be useful in preparing polyurethane prepolymers, i.e. urethane polymers of relatively low molecular weight which are supplied to end-users for curing into polyurethane articles or compositions of higher molecular weight.

The catalysts are typically added to the isocyanate / alcohol mixture to give a concentration in the range 1×10^{-6} to 5×10^{-3} % by weight.

The catalysts are also useful in epoxy resin manufacture.

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The invention will be further described by way of the following examples and the drawings which are:

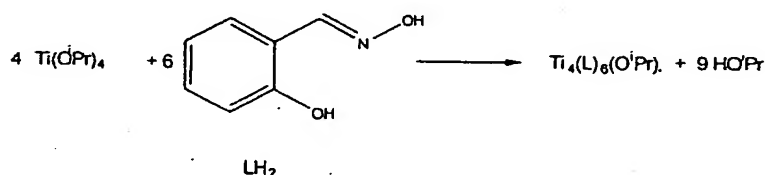
Figure 1: profile of infra-red absorbance peak with time during urethane reaction using catalyst of Example 2(a)

10 Figure 2: as Fig 1, using Example 3 catalyst

Figure 3: as Fig 1, using catalyst of Example 2(c)

Figure 4: as Fig 1, using commercial tin catalyst.

Example 1 Preparation of a titanium-oxime complex



15

Dry toluene (15ml) was added to a Schlenk tube containing salicylaldehyde (2.06g, 15mmol) under an inert atmosphere. Titanium tetraisopropoxide (3ml, 10mmol) was added to this suspension under a positive pressure of argon from a dry syringe. This addition resulted in the immediate formation of an orange solid, which did not enter solution on

20 heating to reflux. The solid was recovered by filtration and found to be soluble only in dimethyl sulphoxide (DMSO). On reduction in volume *in vacuo* the remaining solution yielded X-ray quality crystals of $\text{Ti}_4(\text{L})_6(\text{O}^i\text{Pr})_4$, hexa(salicylaldomiminato)tetraisopropoxy titanate. Yield = 2.6g (84%), melting point = $145-147^\circ\text{C}$. The structure of the crystalline product was confirmed using ^1H NMR at 400MHz in deuterated DMSO and by single-crystal

25 X-ray diffraction studies.

Example 1(b) preparation of bis(salicylaldoximinato)octaisopropoxy titanate

Dry Toluene (10ml) was added to a Schlenk containing salicylaldehyde (2.06g, 15mmol) under an inert atmosphere. Titanium tetraisopropoxide (6ml, 20mmol) was added to the

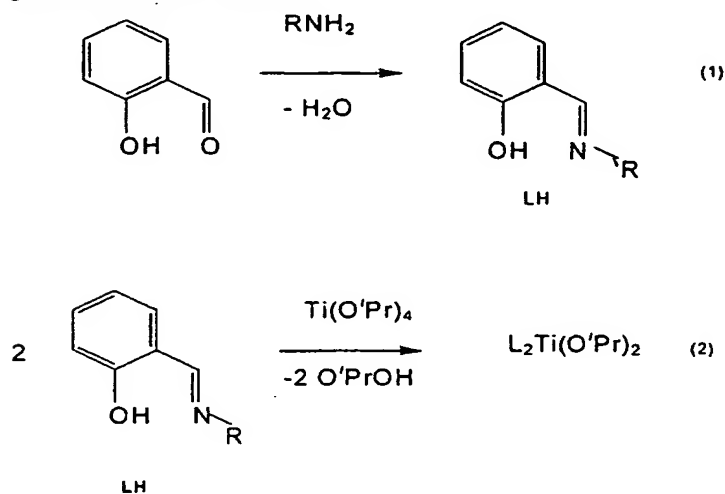
30 resulting suspension resulting in the formation of an orange solution. The volume of this solution was reduced *in vacuo* to approximately half of its original volume and left to stand. After standing for 24 hours the solution yielded a crop of orange crystals of $\text{Ti}_3(\text{L})_2(\text{O}^i\text{Pr})_8$ bis(salicylaldoximinato)octaisopropoxy titanate where L represents the ligand derived from salicylaldehyde. The yield = 1.86g (31.5%), melting point = $146-148^\circ\text{C}$. The structure of the

crystalline product was confirmed using ^1H NMR at 400MHz in CDCl_3 and by single-crystal X-ray diffraction studies

Example 2(a) Preparation of a titanium-Schiff base complex bis(salicylaldiminato)

5 octaisopropoxy titanate

Schiff base ligands (LH) were prepared as described by S.Chong, L. Jones II, C. Wong, L. M. Henling, R. H. Grubbs, *Organometallics* (1998) 17, 3460 according to the following general reaction scheme:



10 (i) Preparation of salicylaldimine

Salicyl aldehyde (10ml, 11.46g, 93.83mmol) and phenyl aniline (9ml, 9.20g, 98.75mmol) was dissolved in toluene (100ml) and a catalytic amount of para-toluene sulfonic acid was added. After heating at reflux temperature on a Dean-Stark apparatus over night, the mixture was cooled down and the solvent removed in vacuo. The remaining oil was dissolved in dichloromethane, the solution washed with water and dried over sodium sulphate. Removal of the filtered solvent gave a yellow oil which solidified on standing. The yield was 16.30g (88%) and the identity of the product was confirmed by ^1H - and ^{13}C -NMR spectroscopy.

20 (ii) Reaction of salicyl aldimine with $\text{Ti}(\text{O}^i\text{Pr})_4$

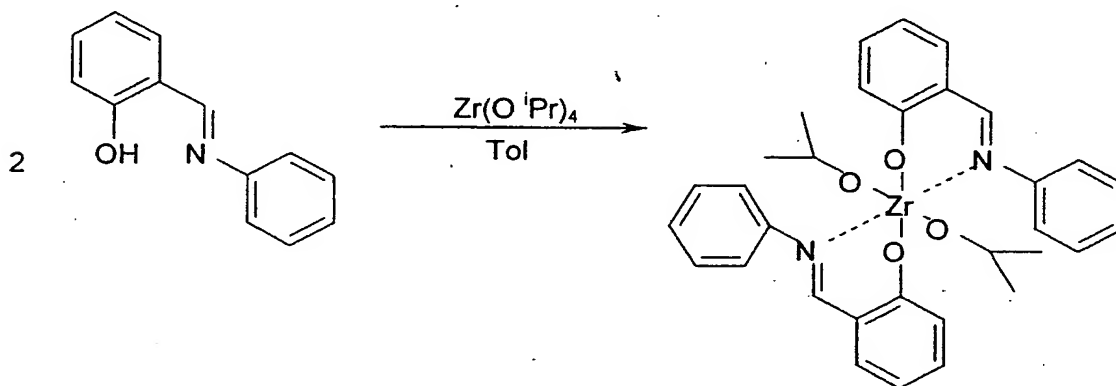
Dry toluene (30ml) was added to a Schlenk tube containing phenylsalicylaldimine, (6 mmol, 1.18 g,) under an inert atmosphere to give a suspension at room temperature. To this suspension was added titanium tetraisopropoxide (3 mmol, 0.9 ml) under a positive pressure of argon using a dry syringe. The resulting suspension was heated to reflux and then cooled to room temperature leaving a yellow solution. Solvent was removed in vacuo until the formation of a yellow precipitate. This was then warmed into a yellow solution which yielded a crop of yellow crystals of bis(salicylaldiminato)octaisopropoxy titanate on standing at 5°C for 24 hours. These crystals were isolated under dry argon and washed

with cold, dry hexane prior to analysis (yield 70 %). The structure of the crystalline product was confirmed using ^1H NMR at 400MHz in CDCl_3 and by single-crystal X-ray diffraction studies

5 **Example 2(b)** Preparation of bis(2,6-diisopropylphenylsalicyaldimato)bis(isopropoxy) titanate

The general procedure above was used to prepare bis(2,6-diisopropylphenylsalicyaldimato)bis(isopropoxy) titanate

10 **Example 2(c)** preparation of bis(salicyaldiminato) octaisopropoxy zirconate

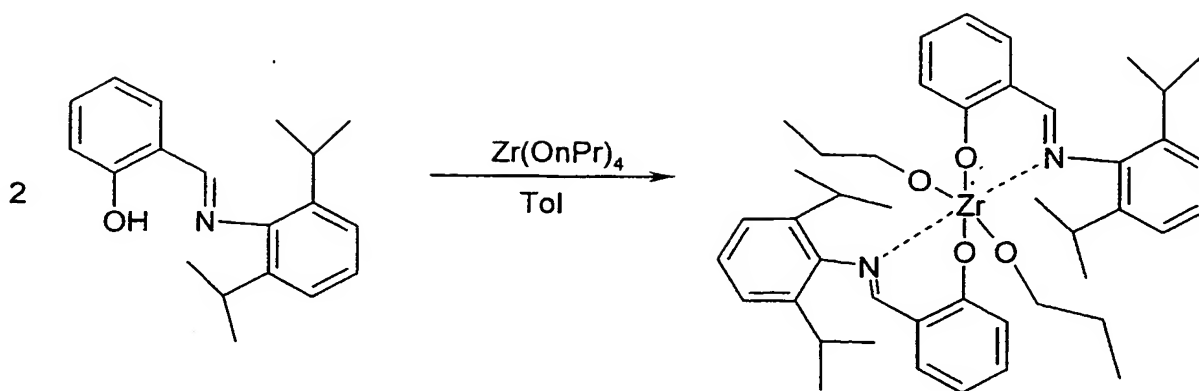


2-(phenylimino-methyl)-phenol (2g, 10.14mmol) was dissolved in dry toluene (10ml) under argon with stirring. Then zirconium(IV) tetraisopropoxide isopropanol complex (2.4g, 6.19mmol) dissolved in toluene (10ml) was added via a canula. After stirring at room

15 temperature for an hour the solvent was removed in vacuo and the remaining solid recrystallised from hexane. Filtration gave 2.02g (66.20% yield) of a yellow solid. Identity was established by ^1H - and ^{13}C -NMR.

20 **Example 2(d)** Reaction of 2-[(2,6-diisopropyl-phenylimino)-methyl]-phenol with zirconium(IV)-n-propoxide

2-[(2,6-diisopropyl-phenylimino)-methyl]-phenol (3g, 10.66mmol) was dissolved in dry toluene (20ml) under argon with stirring. Zirconium(IV)-tetra(n-propoxide) was then added via syringe. After stirring at room temperature for about an hour the solvent was removed in vacuo and the residue recrystallised from hexane to give yellow crystals (yield: 2.71g
25 (66%) which were identified by ^1H - and ^{13}C -NMR spectroscopy as well as by crystal structure.



Example 3 Preparation of bis 8-hydroxyquinolate bis isopropanolate complex

- 5 Dry toluene (20ml) was added to a Schlenk tube containing 8-hydroxyquinoline (7.23g, 50mmol) under an inert atmosphere to give a suspension at room temperature. To this suspension was added titanium tetraisopropoxide (7.5ml, 7.11g, 25mmol) under a positive pressure of argon using a dry syringe. Formation of a yellow suspension occurred immediately and this was stirred for approximately 1 hour. On heating to reflux an
- 10 orange/yellow solution was formed which on cooling yielded a crop of yellow crystals of bis 8-hydroxyquinolate bis isopropanolate. Yield = 8.02g (71%) Melting Point = 184-185°C. The structure of the crystalline product was confirmed using ¹H NMR at 400MHz in deuterated DMSO and by single-crystal X-ray diffraction studies

15 **Example 4** Preparation of titanium- 8-hydroxyquinolate complex with replaced alkoxide

Preparation of titanium bis 8-hydroxyquinolate bis phenolate

- Dry toluene (50ml) was added to a Schlenk tube containing titanium bis 8-hydroxyquinolate bis isopropanolate, (4.59g, 10mmol) and phenol (1.88g, 20mmol) under an inert atmosphere. The resulting orange/yellow suspension was heated at reflux for 20
- 20 hours to give an orange solution. Approximately 50% of the solvent was removed *in vacuo* and the resulting suspension heated to give a solution. On cooling to ambient temperature this solution yielded a crop of orange crystals of titanium bis 8-hydroxyquinolate bis phenolate. Yield = 4.33g (82%), melting point = 207-209°C.

25 **Example 5** Use of Ti complexes of the invention as catalysts

A model urethane reaction, between methylene diphenyldiisocyanate (MDI) and 2-methoxyethanol was used to determine and compare the catalytic activity of the titanium complexes of the invention.

- 30 MDI was purified by dissolving in toluene and removing insoluble material by filtration and then removing the solvent. The MDI produced was found to be analytically pure by NMR

and was stored at -80°C . A standard 0.75M solution of MDI was prepared by dissolving 4.69g of purified MDI in dry degassed C_6D_6 in a 25 ml volumetric flask. The resulting clear solution was stored under argon over molecular sieves. 2-methoxyethanol was degassed and stored under argon over molecular sieves. C_6D_6 was dried over molecular sieves,
 5 degassed and stored under argon.

For each catalyst tested, a standard catalyst solution was prepared using inert atmosphere techniques. First a solution was prepared in 5ml of C_6D_6 to give an approximate molarity of $5 \times 10^{-2} \text{ mol l}^{-1}$, based on the concentration of titanium atoms. This solution was then diluted
 10 in C_6D_6 benzene to give an approximate molarity of $1.25 \times 10^{-3} \text{ mol l}^{-1}$. The catalyst solution was stored under argon at -10°C .

The reactions were carried out under an atmosphere of argon. A Schlenk tube was charged with 3.5ml of 2-methoxyethanol (0.0476 moles). To this was added x ml of catalyst
 15 solution and 1.25-x ml of C_6D_6 . At starting time t_0 , 2.5 ml of standard MDI solution (1.875×10^{-3} moles) were added. A sample of the solution was removed under argon and transferred to a clean, dry NMR tube, which was filled with argon. The tube was sealed under an argon atmosphere and NMR spectra were taken at regular intervals until
 20 approximately 80% of the MDI starting material could be seen to have disappeared. To maintain pseudo-first order conditions, in all experiments the alcohol was maintained as a minimum 1000-fold excess with respect to MDI, and a minimum 25000-fold excess with respect to catalyst.

Kinetic data was obtained by monitoring the disappearance of the signals due to the
 25 aromatic protons of the starting MDI (6.6 - 6.85ppm) and the concomitant appearance of the signals for the aromatic protons of the new urethane product (6.85 - 6.96 and 7.35 - 7.55ppm).

Table 1

Catalyst	Relative rate
Example 2a	1
Example 1b	0.595
Example 2b	0.345
Example 3	0.102

30 The percentage of MDI remaining at the time at which each spectrum was taken was determined by calculating the ratio of integral of the starting material peaks to the total integral of peaks due to both starting materials and products in both these regions. The natural log of the MDI concentration was plotted against time to give in all cases a straight line whose gradient was equal to $-k_{\text{obs}}$. A plot of k_{obs} versus catalyst concentration

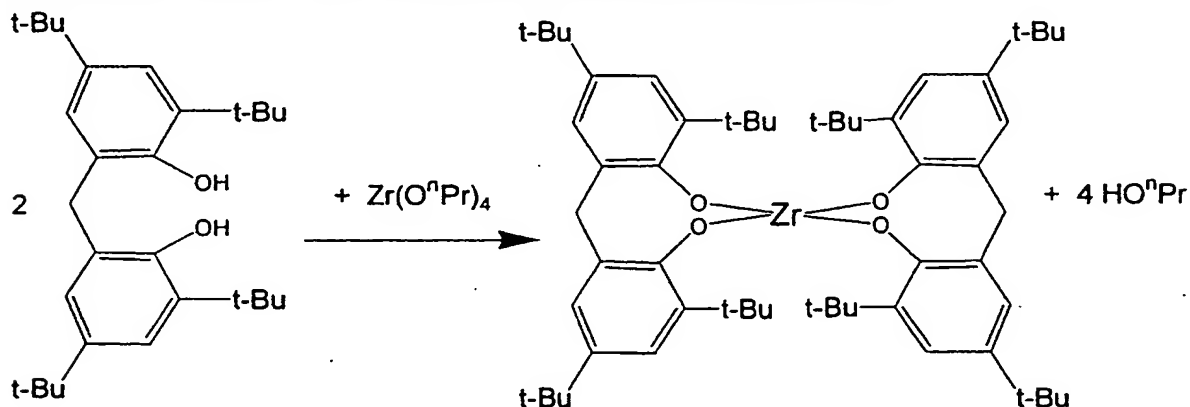
was then produced which gave a straight line. Comparison of the gradients of the lines obtained from these final plots of k_{obs} vs. $[Ti]$ for each catalyst allowed the relative rates of each catalyst for these reactions to be assessed. The results are shown in Table 1.

5 Example 6 Formation of metal complexes with substituted phenols

Example 6(a) Titanium 2,2'methylene bis (6-*t*-butyl-4-methyl phenolate) bis isopropanolate
Dry toluene (10ml) was added to a Schlenk tube containing 2,2'methylene bis (6-*tert*-butyl-4-methyl phenol) (3.41g, 10mmol) under an inert atmosphere. To this suspension was
10 added titanium tetraisopropoxide (3.0ml, 10mmol) under a positive pressure of argon using a dry syringe. The resulting red/brown suspension was heated to form a red solution, which on cooling yielded Ti 2,2'methylene bis (6-*tert*-butyl-4-methyl phenolate) bis isopropanolate as a crop of red crystals. Yield = 2.83g (56%), melting point = 83-85°C. The structure of the crystalline product was confirmed using 1H NMR at 400MHz in $CDCl_3$

Example 6(b) Titanium 2,2'ethyldiene bis (4,6-di-*tert*-butyl phenolate) bis isopropanolate
Dry toluene (10ml) was added to a Schlenk tube containing 2,2'ethyldiene bis (5,6-di-*tert*-butyl phenol) (4.39g, 10mmol) under an inert atmosphere. To this suspension was added titanium tetraisopropoxide (3.0ml, 10mmol) under a positive pressure of argon using a dry
20 syringe. The resulting orange suspension was heated with stirring until the solid had entirely entered solution. On cooling to ambient temperature the solution yielded Ti2,2'ethyldiene bis (4,6-di-*tert*-butyl phenolate) bis isopropanolate as a crop of bright orange crystals. Yield = 3.33g (55.3%), melting point = 94-96°C. The structure of the crystalline product was confirmed using 1H NMR at 400MHz in $CDCl_3$

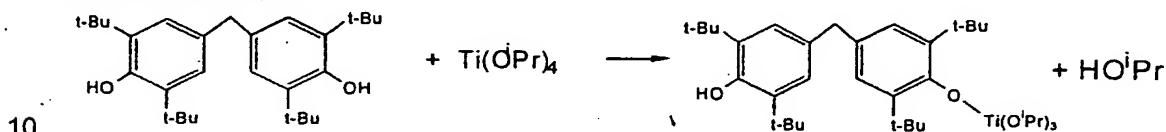
Example 6(c) Zirconium bis 2,2'ethyldiene bis (4,6-di-*tert*-butyl phenolate)



Dry toluene (5ml) was added to a Schlenk tube containing 2,2'ethyldiene bis (5,6-di-*tert*-butyl phenol) (2.20g, 5mmol) under an inert atmosphere. To this suspension was added
30 zirconium tetra-*n*-propoxide (1.7ml, 5mmol) under a positive pressure of argon using a dry

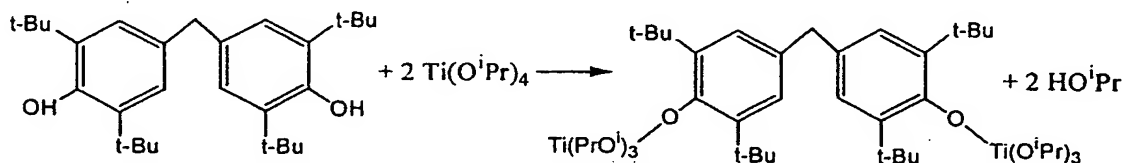
- syringe. Precipitation occurred immediately and the solvent was removed *in vacuo* to leave a white solid. Dry THF (5ml) was added to this solid and the resulting suspension heated to reflux to give a pale yellow solution which on standing yielded Zr bis 2,2' ethylidene bis (4,6-di-*tert*-butyl phenolate) as a crop of clear crystals. Yield = 1.32g (55% based on the ligand)
- 5 Melting point 185°C (dec.) The structure of the crystalline product was confirmed using ¹H NMR at 400MHz in CDCl₃

Example 6(d) Titanium 4,4' methylene-(2,6-di-*tert*-butyl phenol)(2,6 di-*tert*-butyl phenolate) tris isopropanolate



- Dry hexane (5ml) was added to a Schlenk tube containing 4,4' methylene bis (2,6-di-*tert*-butyl phenol) (2.12g, 5mmol) under an inert atmosphere. Titanium tetraisopropoxide (1.5ml, 5mmol) was added to this suspension under a positive pressure of argon using a dry syringe. A yellow solution was formed immediately. Approximately 50% of the solvent
- 15 was removed *in vacuo* and the remaining yellow solution was placed in the freezer. On standing at this temperature for 24 hours a large amount of a yellow product precipitated from solution and was isolated. Yield = 2.02g (62.4%). The structure of the crystalline product was confirmed using ¹H NMR at 400MHz in CDCl₃

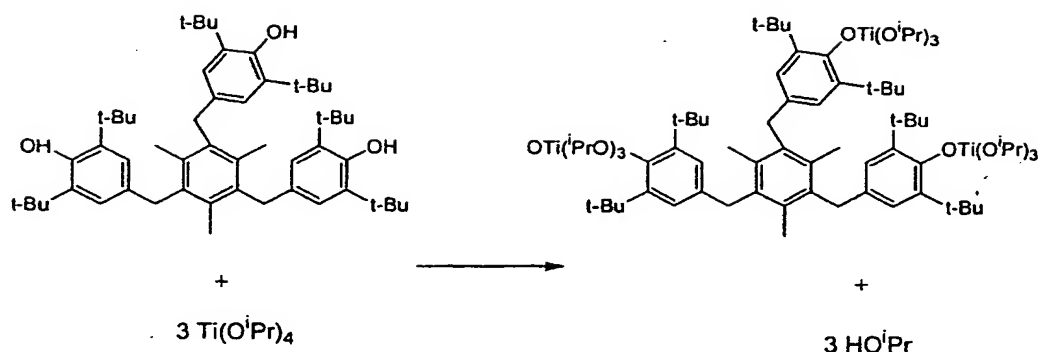
20 Example 6(e) 4,4'-methylene bis(2,6 di-*tert*-butylphenolate) bis titanium tris isopropanolate



- Dry hexane (5ml) was added to a Schlenk tube containing 4,4' methylene bis (2,6-di-*tert*-butyl phenol) (2.12g, 5mmol) under an inert atmosphere. Titanium tetraisopropoxide (3.0ml, 10mmol) was added to this suspension under a positive pressure of argon using a dry
- 25 syringe. A yellow solution was formed immediately. Approximately 50% of the solvent was removed *in vacuo* and the remaining yellow solution was placed in the fridge. On standing at this temperature for 24 hours a large amount of a yellow fibrous product, 4,4'-methylene bis(2,6 di-*tert*-butylphenolate) bis titanium tris isopropanolate, precipitated from solution and was isolated. Yield = 3.12g (71.6%), melting point = 75-77°C. The structure of the
- 30 crystalline product was confirmed using ¹H NMR at 400MHz in CDCl₃

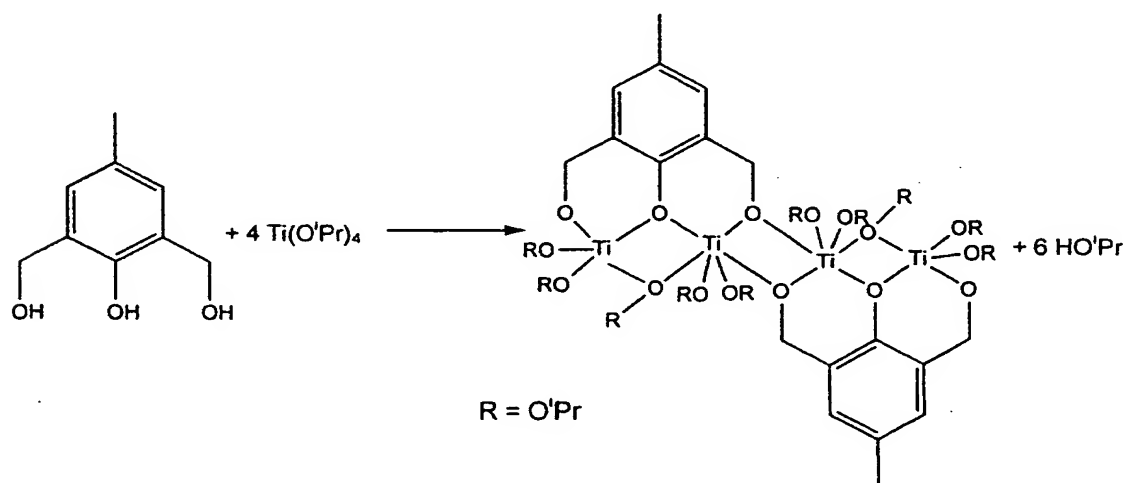
Example 6(f) Complex between three equivalents of titanium isopropoxide and 1,3,5-trimethyl-2-4-6-tris (3,5-di-*tert*-butyl-4-hydroxybenzyl) benzene

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Dry hexane (15ml) was added to a Schlenk tube containing 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (3.88g, 5mmol) under an inert atmosphere. To this suspension was added titanium tetraisopropoxide (4.5ml, 15mmol) under a positive pressure of argon from a dry syringe. A pale yellow solution was formed immediately. Approximately 50% of the solvent was removed *in vacuo* and the resulting solution placed in the freezer. On standing for 24 hours in the freezer the solution yielded 10 as a crop of yellow/white crystals which re-dissolved on warming to room temperature. The crystals were recovered by filtration at 0°C but a significant amount was lost due to their high solubility. The yield = 1.8g (24.9%) melting point = 183-185°C. The structure of the crystalline product was confirmed using ¹H NMR at 400MHz in CDCl₃ and by single-crystal X-ray diffraction studies.

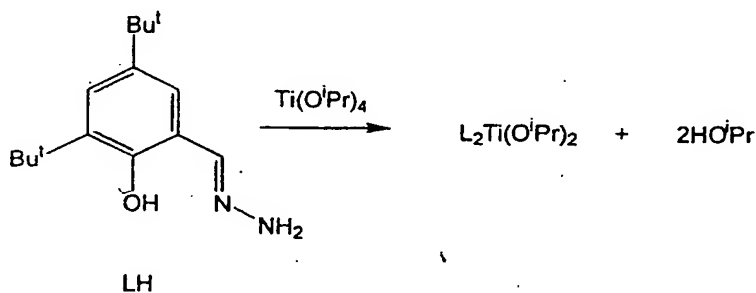
Example 6(g) Complex between titanium tetra isopropoxide and 2,6 bis hydroxymethyl-p-cresol



Dry hexane (10ml) was added to a Schlenk tube containing 2,6 bis hydroxymethyl-p-cresol (1.68g, 10mmol) under an inert atmosphere. To this suspension was added titanium tetraisopropoxide (6.0ml, 20mmol) under a positive pressure of argon from a dry syringe. This resulted in the formation of an orange brown suspension that was filtered to leave a pale orange solution and left to stand for 24 hours. This solution yielded a crop of small,

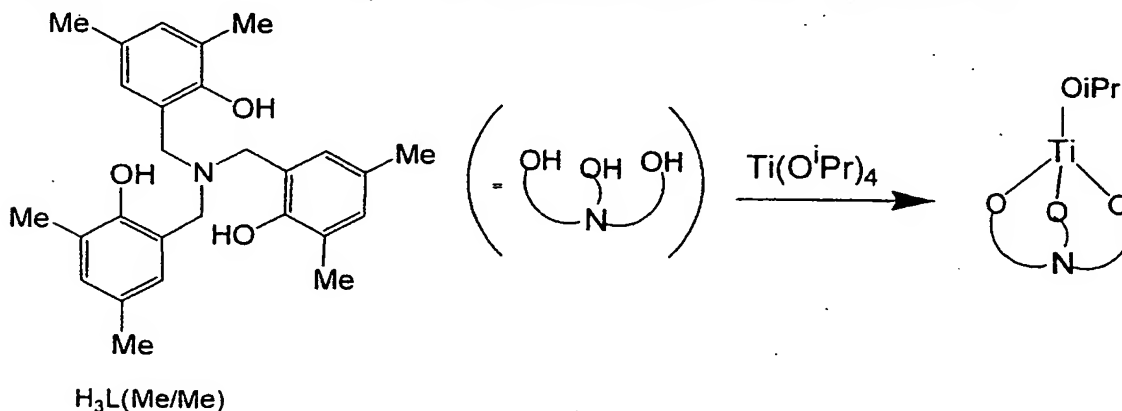
clear crystals of the product. The yield = 3.80g (34.2%), melting point = 94-97°C. The structure of the crystalline product was confirmed using ^1H NMR at 400MHz in CDCl_3 and by single-crystal X-ray diffraction studies.

5 Example 7 Preparation of bis(2,4-di-tert-butyl-salicylaldehyde hydrazoneato)bis(isopropoxy) titanate



- Dry toluene (10ml) was added to a Schlenk tube containing 2,4-di-tert-butyl-salicylaldehyde hydrazone, 2 mmol, 0.5 g,) under an inert atmosphere to give a suspension at room temperature. To this suspension was added titanium tetraisopropoxide (1 mmol, 0.3 ml) under a positive pressure of argon using a dry syringe. The resulting suspension was heated to reflux and then cooled to room temperature leaving a yellow solution. Solvent was removed in vacuo until the formation of a yellow precipitate. This was then warmed into a yellow solution which yielded a crop of yellow crystals of bis(2,4-di-tert-butyl-salicylaldehyde hydrazoneato)bis(isopropoxy) titanate on standing at 5 °C for 24 hours. These crystals were isolated under dry argon and washed with cold, dry hexane prior to analysis (yield 73 %). The structure of the product was confirmed using ^1H NMR at 400MHz in CDCl_3 and by single-crystal X-ray diffraction studies.

20 Example 8 Preparation of titanium isopropoxide derivative of an aminotrisphenolate



$\text{Ti}(\text{OiPr})_4$ (3.1ml, 10mmol) was added dropwise by syringe, to a stirred suspension of $\text{H}_3\text{L}(\text{Me}/\text{Me})$ (4.2g, 10mmol) in toluene (50ml) at 0°C. The reaction mixture was allowed to warm to room temperature, with stirring, resulting in a yellow solution. Removal of solvent

under reduced pressure resulted in the precipitation of a yellow residue, which was re-dissolved in a minimum of fresh hexane (20ml), with heating. The solution has filtered hot to remove insoluble residues. A yellow crystalline solid was obtained on standing for 3hrs at 0°C. The solid was collected by filtration, washed with cold hexane, and dried in vacuo.

- 5 Yield: 4.6g, 88%. The structure was confirmed by ¹H and ¹³C NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction.

Example 9 Preparation of polyurethane prepolymers

- Polypropylene glycol (nominal mol wt = 4000) (100g) was blended with 4,4-methylene bis(phenylisocyanate) (35g) and the mixture stirred and heated to 80 °C. Catalyst was then added at an amount of 3.14×10^{-3} parts by weight of the mixture. The mixture was analysed by in-situ infra-red spectroscopy every minute following catalyst addition. The size of the peaks resulting from absorbances of the isocyanate groups of the isocyanate reactant at about 2272 cm⁻¹ and carbonyl groups in the urethane bonds formed (at about 1730 cm⁻¹) were recorded and are shown in Figs 1 - 3. The results using the catalysts made in Examples 2(a), 2(c) and 3 are shown in Figs 1-3. Fig 4 shows the same experiment using commercially available dibutyltin dilaurate catalyst added at the same concentration of metal as a comparison.

- 20 The results show that using the catalysts of Examples 2(a) (in Fig 1), 2(c) (in Fig 3) and 3 (in Fig 2) there is a rapid decrease in NCO groups in the mixture which correlates with a rapid increase in the number of urethane carbonyls, showing a rapid formation of urethane groups in the mixture as polyurethane is formed. The reaction using the tin catalyst is much less rapid.

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The amount of NCO groups in the reaction mixture before addition of catalyst and after three hours was measured by neutralising the NCO groups in the mixture with excess dibutylamine and then titrating the remaining dibutylamine with HCl. The results are shown in Table 2.

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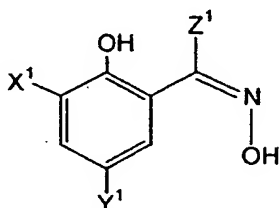
Table 2

Catalyst	Initial NCO (% by weight)	Final NCO (% by weight)
Example 2(a)	7.84	*NR
Example 3	7.84	*NR
Dibutyltin dilaurate (comp)	7.84	3.79
None (comp)	7.84	5.37

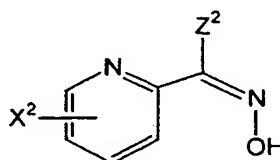
The mixtures containing the catalysts of the invention were too viscous to analyse using this method, showing that a high degree of polymerisation had occurred.

Claims

1. A compound suitable for use as a catalyst for the formation of urethanes, ureas and epoxy resins comprising the reaction product of
 - (i) an alkoxide, condensed alkoxide or halo-alkoxide of titanium zirconium, hafnium or aluminium or a mixture thereof, and
 - (ii) a complexing compound having a hydroxy group which is capable of reacting with the metal compound of (i) and which is selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols.
2. A compound as claimed in claim 1, wherein the complexing compound is an aryl-substituted (including polycyclic aryl-), aromatic or heterocyclic oxime of Formula 1 or Formula 2,



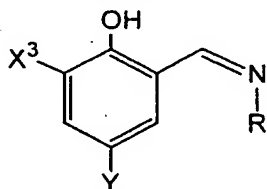
Formula 1



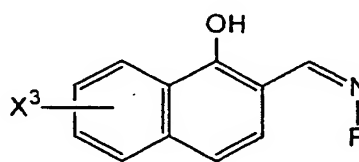
Formula 2

in which X¹, Y¹ and X² which may be the same or different, are selected from H, alkyl, alkoxy, NO₂, halogen, amino (including alkylamino) and Z¹ or Z² is selected from H, or an alkyl aryl or pyridyl group, any of which may be substituted or unsubstituted.

3. A compound as claimed in claim 1, wherein the complexing compound is a hydroxy-Schiff base of general Formula 3 or 3a,



Formula 3



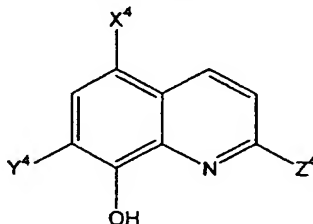
Formula 3a

where X³ and Y³ are selected from H, alkyl, alkoxy, NO₂, halogen, amino (including alkylamino) and R is substituted or unsubstituted alkyl, including cycloalkyl, aryl, aryloxy, alkoxy, or a polycyclic group such as quinolyl.

4. A compound as claimed in claim 3 wherein the hydroxy Schiff base is a dimeric or trimeric Schiff base, in which R in Formula 3 or 3a comprises a linking group which is linked

to a second or third Schiff base moiety and said linking group contains between 1 and 6 atoms which comprise one or more of C, N and O.

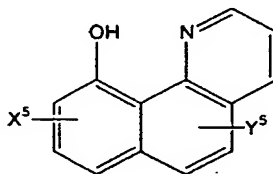
5. A compound as claimed in claim 1, wherein the complexing compound is a 8-hydroxyquinoline derivative of the general formula 4:



Formula 4

where X^4 and Y^4 are each independently selected from H, halogen, NO_2 , alkyl or alkenyl and Z^4 is H or alkyl.

6. A compound as claimed in claim 1, wherein the complexing compound is a 10-hydroxybenzo-[h]-quinoline derivative of the general formula 5:



Formula 5

where X^5 and Y^5 are, independently, selected from H, halogen, NO_2 , alkyl or alkenyl.

7. A compound as claimed in claim 1, wherein the complexing compound is an aromatic hydrazone, which may be unsubstituted or substituted at either the aromatic ring or the N atom.

8. A compound as claimed in claim 1, wherein the complexing compound is a substituted phenol having a substituent which includes a N-, O- or S- containing group which can coordinate to a metal atom.

9. A catalyst composition comprising a compound as claimed in any of claims 1 to 8.

10. A curable composition comprising at least one polyisocyanate compound, a compound which is capable of reacting with said polyisocyanate compound to form a polymer and a catalyst composition as claimed in claim 9.

11. The use of a compound as claimed in any of claims 1 – 8 as a catalyst in the reaction of an isocyanate compound with either a hydroxyl-containing compound or an amine-containing compound to form a urethane or urea compound respectively.

12. A method of making a catalyst compound, suitable for catalysing the reaction of an isocyanate compound with either a hydroxyl-containing compound or an amine-containing compound to form a urethane or urea compound respectively, comprising the steps of:

- (i) forming a solution of a complexing compound which is selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols,
- (ii) mixing said solution with an alkoxide, condensed alkoxide or halo-alkoxide of titanium, zirconium, hafnium or aluminium, and
- (iii) optionally heating said mixture to reflux.

AMENDED CLAIMS

**[Received by the International Bureau on 30 January 2003 (30.01.03):
original claims 1-12 unchanged; new claims 13-14 added (1 page)]**

11. The use of a compound as claimed in any of claims 1 – 8 as a catalyst in the reaction of an isocyanate compound with either a hydroxyl-containing compound or an amine-containing compound to form a urethane or urea compound respectively.

12. A method of making a catalyst compound, suitable for catalysing the reaction of an isocyanate compound with either a hydroxyl-containing compound or an amine-containing compound to form a urethane or urea compound respectively, comprising the steps of:

- (i) forming a solution of a complexing compound which is selected from the list comprising oximes, hydroxy-Schiff bases, 8-hydroxyquinoline derivatives, 10-hydroxybenzo-[h]-quinoline derivatives, hydrazones and substituted phenols,
- (ii) mixing said solution with an alkoxide, condensed alkoxide or halo-alkoxide of titanium, zirconium, hafnium or aluminium, and
- (iii) optionally heating said mixture to reflux.

13. A curable composition comprising an epoxy group-containing compound, a compound having a hydroxy or amine group which is capable of reacting with said epoxy group-containing compound to form an epoxy resin and a catalyst composition as claimed in claim 9.

14. The use of a compound as claimed in any of claims 1 – 8 as a catalyst in the manufacture of an epoxy resin.

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Figure 1: Catalyst of Example 2(a)

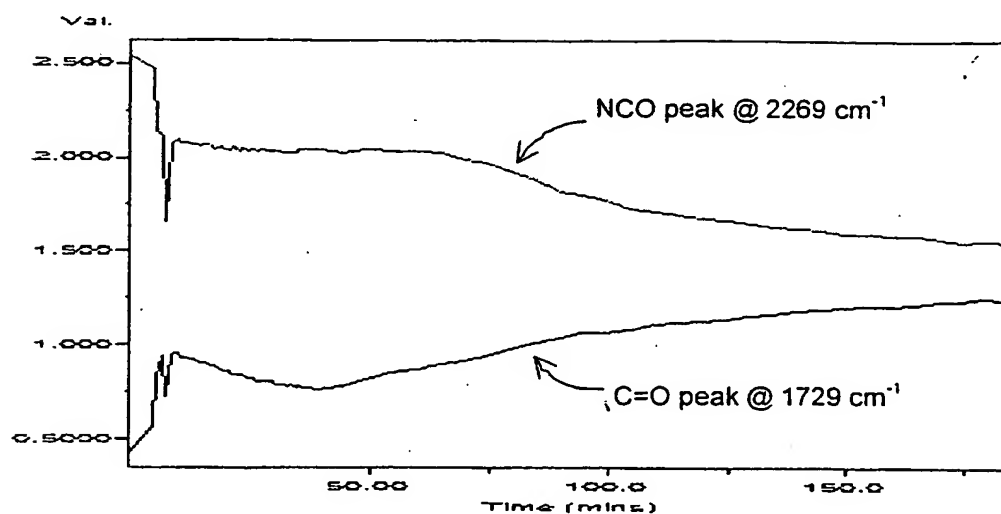
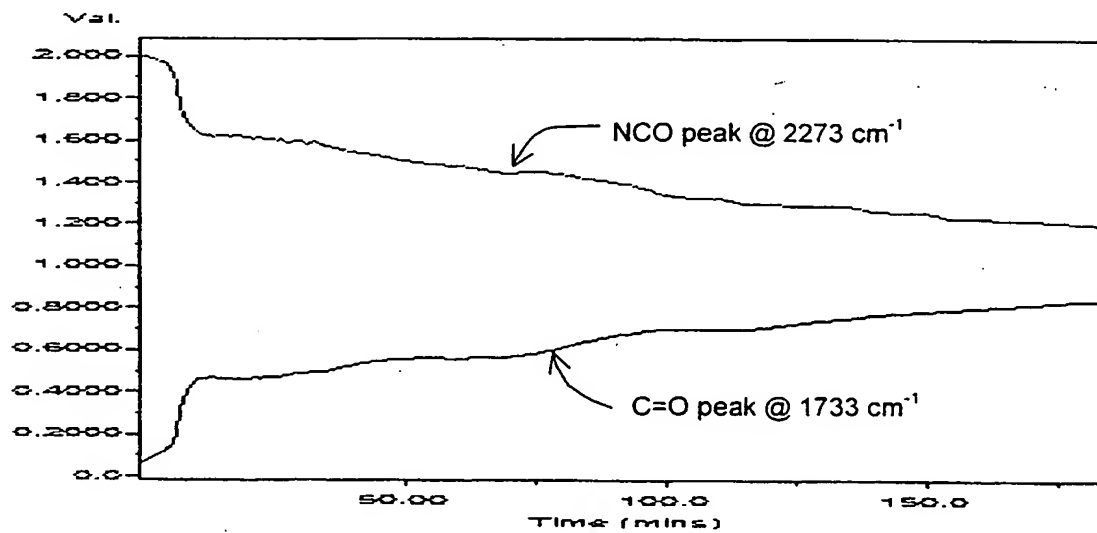


Figure 2: Catalyst of Example 3



2/2

Fig 3 Catalyst of Example 2(c)

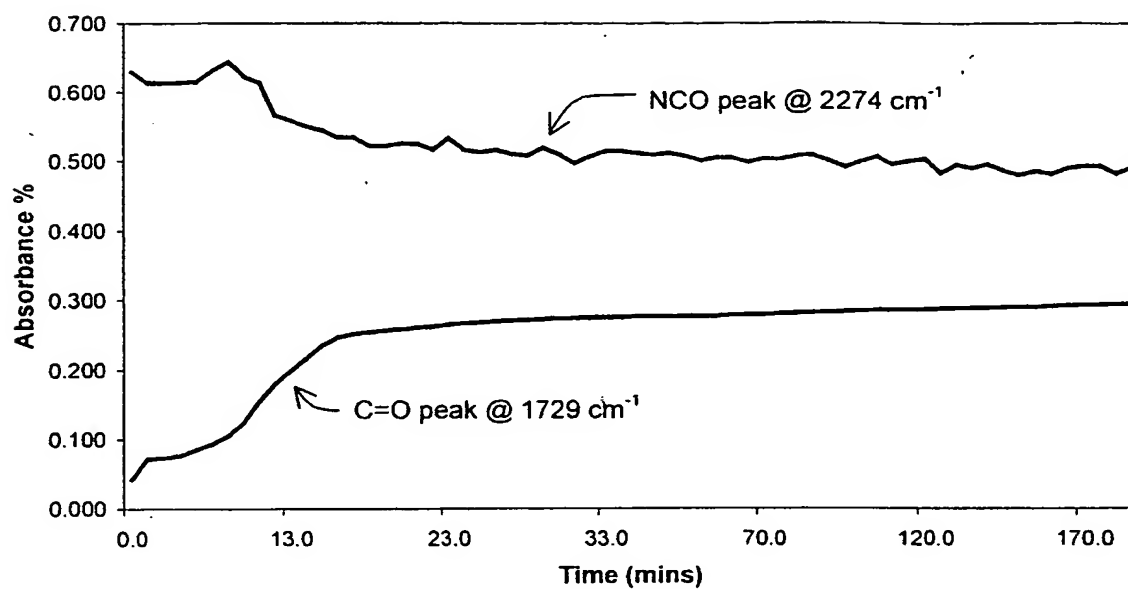
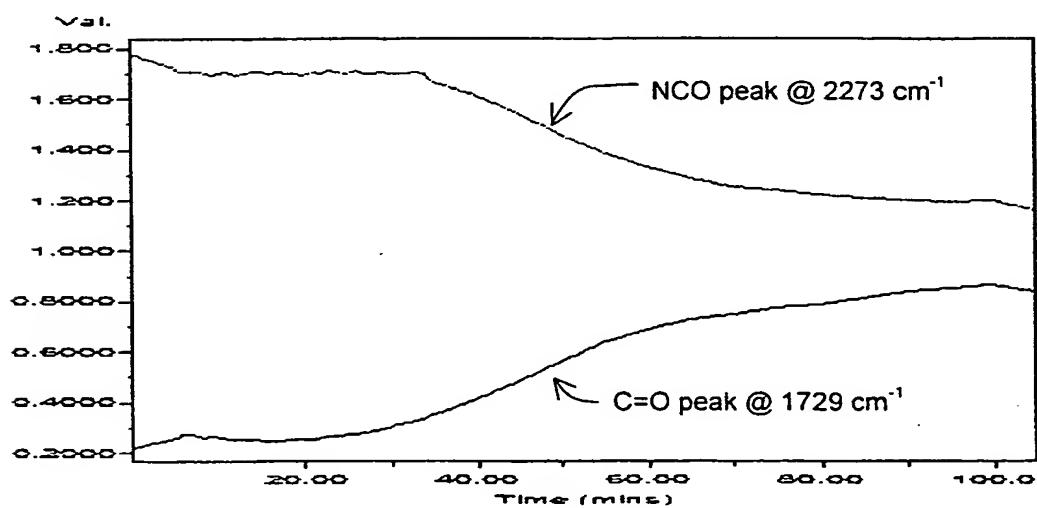


Fig 4: Comparison using tin catalyst



INTERNATIONAL SEARCH REPORT

PCT/GB 02/03896

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/22 B01J31/22 C09D175/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G B01J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SINGH A ET AL: "REACTIONS OF OXIMES AND DIETHYLHYDROXYLAMINE WITH TITANIUM ALKOXIDES" JOURNAL OF THE CHEMICAL SOCIETY, SECTION A: INORGANIC, PHYSICAL AND THEORETICAL CHEMISTRY, CHEMICAL SOCIETY. LETCHWORTH, GB, vol. 15, 1971, pages 2440-2444, XP001073925 the whole document	1-9
X	US 3 055 847 A (IVERSON MARLOWE L ET AL) 25 September 1962 (1962-09-25) column 1, line 28 - line 40 -/--	1,8

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

PCT/GB 02/03896

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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